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Formation and isomerization of C_{120}: considerations of symmetry, kinetics and thermodynamics†

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ABSTRACT: An orbital-symmetry analysis (OCAMS) of the dimerization of C_{60} to its stable (D_{2h}) dimer **1** indicates that the reaction cannot proceed along a totally symmetric pathway but that the reaction-path symmetry must be reduced at least to C_{2h}. Similarly, one-step conversion of **1** to its isomer **3** (also D_{2h}), which has been proposed as an intermediate for the intercalation of helium atoms into C_{60}, is also limited to a C_{2h} pathway. As neither of these pathways is geometrically appropriate, it is predicted that both reactions proceed stepwise. Semi-empirical computations (AM1/UHF) confirmed this prediction: in the dimerization, a transoid singlet biradical (**2**) is formed, and then closes readily to **1** after rotation about its newly formed bond. An intermediate (**4**) of C_{2v} symmetry is detected along the pathway for isomerization of **1** to **3**. THERMO computations (AM1/RHF) indicated that both dimers should be in thermal equilibrium with C_{60} at moderate temperatures, but that their equilibrium concentrations in the gas phase would be exceedingly small under thermally accessible conditions. The limitations of the computational method employed and their bearing on the reliability of the results are discussed.

KEYWORDS: fullerenes; dimers of C_{60}; isomerization of C_{120}; thermodynamics of carbon clusters

INTRODUCTION

The existence of a number of stable C_{120} isomers has been predicted computationally. The literature has been summarized by Patchkovski and Thiel, who carried out an exhaustive mapping of the potential energy surface.[1] In a recent publication,[2] the present author applied criteria of orbital symmetry conservation[3] to the dimerization of C_{60}, and traced the reaction path by means of point-by-point semi-empirical (AM1/UHF) computations.

It was observed that the results of pathway computations carried out under specific symmetry restrictions varied to some extent from those performed with full optimization, so the stationary points were fully optimized. However, the deviations observed along the pathway were disturbing, although they did not affect the qualitative conclusions.[2a]

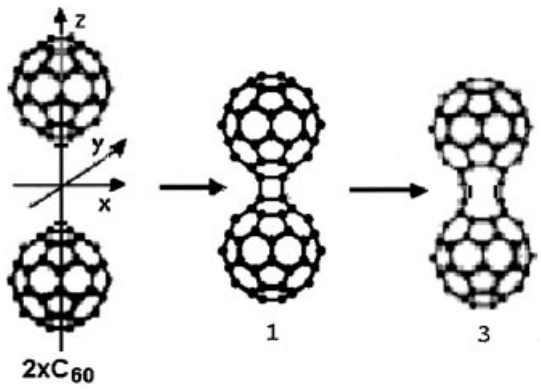
A symmetry analysis was also applied to the isomerization of **1** to a second (D_{2h}) isomer **3**, the 'window' isomer that Patchkovskii and Thiel suggested as a possible intermediate in the intercalation of helium atoms into C_{60}. Regrettably, this latter analysis was in error and had to be corrected in an Erratum.[2b]

In this paper both reactions will be considered systematically, first by orbital-symmetry analysis, then by reaction-path computations with full optimization. Finally, thermodynamic considerations were taken into account.

RESULTS AND DISCUSSION

Symmetry considerations

As illustrated in Scheme 1, the dimerization looks like a suprafacial [2 + 2]-cycloaddition, which is forbidden by the Woodward–Hoffmann rules. The isomerization is a



Scheme 1

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Table 1. Comparison of electronic configurations in D_{2h}

	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
C_{120} (3)	37	25	29	29	25	35	29	31
C_{120} (1)	37	25	29	29	25	36	29	30
$2 \times C_{60}$	37	25	29	29	25	37	29	29

similarly forbidden [2 + 2]-cycloreversion. In an orbital-symmetry analysis of the prototypical dimerization of ethylene to cyclobutane,[2–4] it was shown that the forbiddenness can be removed by an in-plane displacement away from a strictly rectangular geometry towards a parallelogram, which favors bonding along a diagonal. The resulting transoid single-bonded intermediate then rotates about the new bond to a *cis* conformation before closing to the product.

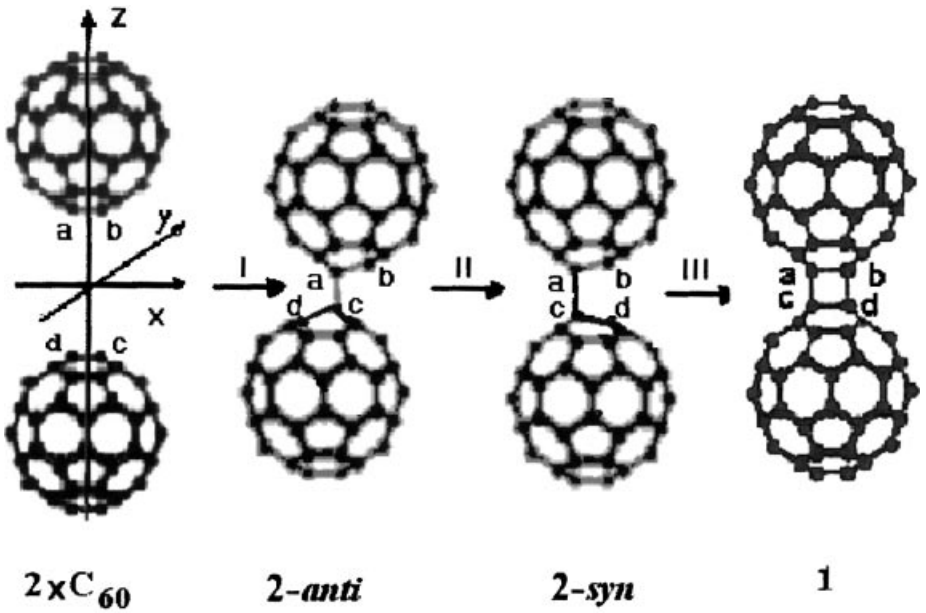
The symmetry analysis is as follows.[2] The reacting monomers and the product dimers are oriented as shown in Scheme 1, with the long axis of the molecule aligned along z and the reacting carbon atoms in the xz-plane. In the dimerization, two π-bonds bisected by the z-axis are transformed to a pair of σ-bonds bisected by the x-axis. Focusing our attention on these bonding changes alone, we would conclude that the dimerization is forbidden in D_{2h} because a doubly occupied molecular orbital of symmetry species b_{1u} in the reactant pair does not correlate with the corresponding doubly occupied b_{3u} orbital of the product. Therefore, the forbiddenness can be removed if a b_{2g} displacement is incorporated into the reaction coordinate, because such a displacement desymmetrizes the pathway from D_{2h} to $C_{2h}^{(y)}$, the kernel of b_{2g}, in which both b_{1u} and b_{3u} map on to b_u. The same reasoning can be applied to the isomerization of **1** to **3**: a b_{2g} displacement along the reaction path formally allows the forbidden transformation of two σ-bonds bisected by the z-axis to a pair of π-bonds bisected by the x-axis.

The predictions of this simple analysis are confirmed when all of the 240 doubly occupied orbitals of the system are taken into account. The electron configurations, i.e. the irreducible representations in D_{2h} of the doubly occupied molecular orbitals, calculated separately with AM1 for a loosely interacting pair of buckyballs and each of the two dimers, are compared in Table 1.

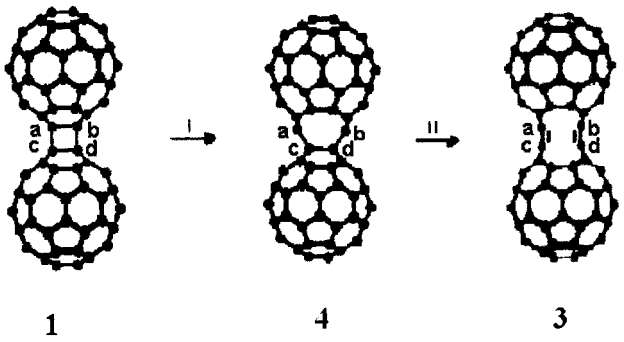
Turning first to the dimerization of $2 \times C_{60}$ to dimer **1**, we see only one mismatch: the monomer pair has one more b_{1u} MO and one less b_{3u} MO than the dimer. As in the simple analysis above, the discrepancy can be removed by a displacement of species b_{2g}. It follows that the pathway via an intermediate of $C_{2h}^{(y)}$ symmetry is allowed. Similarly, the isomerization **1** to **3** involves transfer of a pair of electrons from a b_{1u} orbital in the reactant to a b_{3u} orbital in the product, so a one-step isomerization pathway would also be constrained to $C_{2h}^{(y)}$. Note also that direct dimerization of C_{60} to the 'window' dimer (**3**) would require transfer of two electron pairs from two b_{1u} orbitals to two b_{3u} orbitals, corresponding to concerted rupture of two double bonds and formation of two others—an inherently improbable process.

In keeping with the analysis, semi-empirical pathway computations (AM1/UHF) confirm that dimerization proceeds stepwise via a single-bonded biradical intermediate, **2**. It is formed in a *trans* conformation (C_{2h}), rotates about the newly formed single bond to a near-*cis* conformation (C_{2v}) and closes to the stable dimer **1** (D_{2h}).

The predicted stepwise dimerization mechanism, shown in Scheme 2, is (1) approach along a pathway of



Scheme 2



Scheme 3

essentially $C_{2h}^{(y)}$ symmetry to form the single-bonded intermediate **2**; (2) rotation about the newly formed bond to a near-*cis* conformation [$C_{2v}^{(x)}$], which may or may not be a discrete intermediate, and closure to the stable dimer **1** (D_{2h}).

Prediction of a mechanism for the isomerization of **1** to **3** is more difficult. Patchkovskii and Thiel[1] suggest that rupture of the two bonds is asynchronous, via a structure with $C_{2v}^{(z)}$ symmetry (**4**), which they identified as a transition structure (Scheme 3). This can be brought into agreement with the orbital-symmetry analysis only if the symmetry is reduced further to $C_s^{(zx)}$, the subgroup common to $C_{2v}^{(z)}$ and $C_{2h}^{(y)}$, somewhere along the pathway.

Computational methodology

The previously reported computations, carried out using the MOPAC 93 package with the AM1 hamiltonian, were subject to serious limitations,[2b] the most severe of which is the reliance on the unrestricted Hartee–Fock (UHF) procedure, which is subject to spurious spin polarization when applies to fullerenes.[5]

The single-bonded intermediate in the dimerization (**2**) is a singlet biradical, and the stretched-bond structure **4**, presumed to be on the isomerization pathway, should also have considerable open-shell character. Such species cannot be treated reliably by closed-shell methods and computation at a sufficiently high level of configuration interaction would be excessively time-consuming, so Patchkovskii and Thiel's compromise was to use the MNDO 3 × 3 CI procedure. Computations beyond this minimal level of configuration interaction are prohibitive when it is necessary to calculate a large number of closely spaced points along the reaction path. It was noted that the energy of symmetric structures often differed by several kcal mol^{-1} when calculated with full optimization and when symmetry restrictions were imposed.[2a] Therefore, a full optimization of the remaining 353 internal coordinates was performed for each value of the nominal reaction coordinate. Moreover, in flat regions of the potential energy surface, the gradient norm could only be reduced to an acceptable value by repeating the optimization in cartesiean coordinates. Under the circumstances, UHF seemed to be the only practical option, despite its manifest deficiencies.

Table 2. Heats of formation ($\Delta\Delta H_f$) (kcal mol^{-1}) of the closed shell dimers relative to two molecules of C_{60}

	AM1/RHF	AM1/UHF	MNDO 3 × 3 CI[a]
1 (D_{2h})	−33.1	−42.2	−44.5
3 (D_{2h})	1.4	−6.0	−9.4

[a] Ref. 1

A measure of confidence in the UHF computations can be derived from the fact that the enthalpy differences between the closed-shell dimers **1** and **3** and the separated pair of buckyballs are virtually independent of the computational method. As can be seen in Table 2, both methods place the stable dimer ca 40 kcal mol^{-1} below the monomer pair and the 'window' isomer 34–35 kcal mol^{-1} above its more stable isomer, but still below the isolated monomer pair, which is taken as the reference energy (1 kcal = 4.184 kJ).

Computed reaction pathways

The reaction path for the dimerization is shown in Figs 1 and 2 (the plots in these figures, and also in Figs 3 and 4, are unsmoothed splines; as discussed in Ref. 2a, the points on the pathways are reproducible to within ca 2 kcal mol^{-1}). In the former, in which the nominal reaction coordinate is the distance between the two nearest inter-moiety atoms, the monomers approach one another along an essentially $C_{2h}^{(y)}$ pathway, pass over a barrier of about 17 kcal mol^{-1} and drop to the single-bonded isomer (**2**) in a *trans* conformation, that resides in

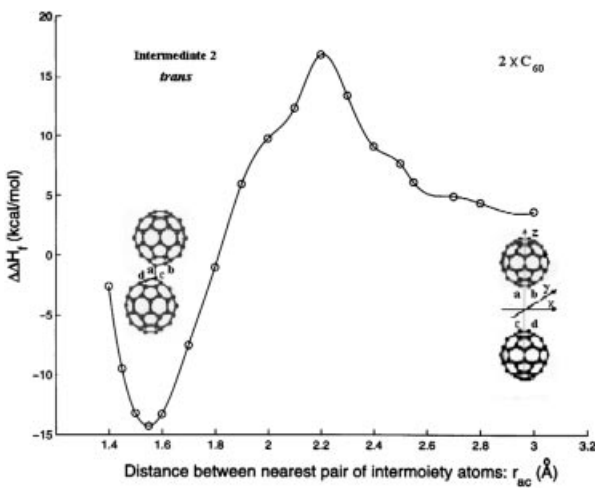


Figure 1. Dimerization: formation of the single-bonded intermediate

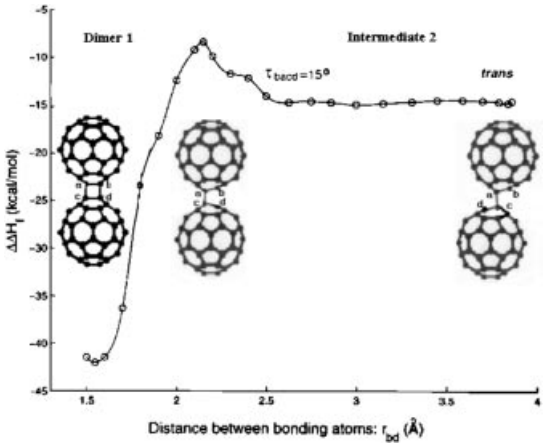


Figure 2. Dimerization: closure of the second bond

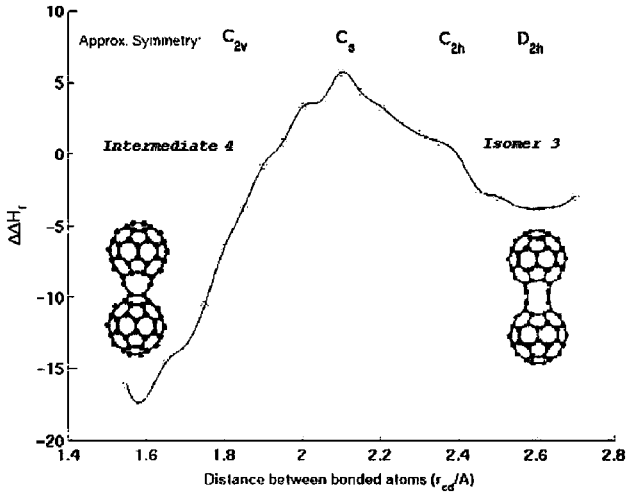


Figure 4. Isomerization: opening of the second bond

a potential well ca 14 kcal mol^{-1} below the monomer pair. In contrast, MNDO 3 × 3 CI locates the transoid single-bonded dimer as a shallow minimum 14.1 kcal mol^{-1} *above* the monomers.[1]

It can be seen in Fig. 2 that internal rotation about the single bond from *trans* towards *cis* is virtually free until the dihedral angle has decreased to about 15°, after which the energy rises to a barrier about 7 kcal mol^{-1} high and drops steeply to dimer **1**. The computed pathway is in agreement with the mechanism outlined in Scheme 2.

As shown in Fig 3 and 4, the isomerization of **1** to **3** is also stepwise, in accord with Scheme 3: rupture of the first bond (Fig. 1) occurs along a $C_{2v}^{(z)}$ pathway, generating a transoid single-bonded dimer (**4**) in a shallow well ca 10 kcal mol^{-1} below **3**. Here too the AM1/UHF results contradict those of MNDO 3 × 3 CI, which locates a similar structure 37 kcal mol^{-1} *above* **3** and characterizes it as a transition state.

As predicted by the symmetry analysis, in the course of the second step (Fig. 4), which involves not only rupture of the second σ-bond but also the formation of two new π-bonds, the symmetry changes from $C_{2v}^{(z)}$ to $C_{2h}^{(y)}$ via their common subgroup C_s before it settles into D_{2h}.

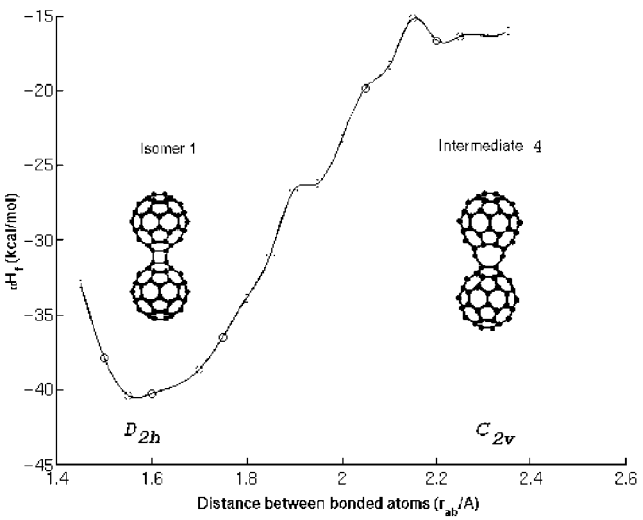


Figure 3. Isomerization: opening of the first bond

The energies computed for the stable and metastable species are listed in Table 3, along with their $<S^2>$ expectation values, the latter [actually $S(S+1)$] being an indication of the degree of spurious spin polarization introduced by the UHF procedure (it should be realized that the numerical value of $<S^2>$ computed by UHF for singlets is meaningless; strictly, $<S^2> = 10.5$ implies that $S = 3$, corresponding to six unpaired electrons!).

As noted above, AM1/UHF and MNDO 3 × 3 CI reduce the energy of the closed-shell molecules to a moderate, very similar extent. In contrast, the energy of the open-shell species is reduced more drastically by the former method than by the latter. This may well be because exaggerated stabilization by spurious spin polarization is more pronounced in open- than in closed-shell species, even though the high $<S^2>$ expectation values are similar across Table 3. Alternatively, it is possible that 3 × 3 CI underestimates the effect of electron correlation in open-shell species, so that computations at a higher level of configuration interaction would reduce the energy further. Pending more sophisticated computations, the author believes that the present results can be regarded as at least qualitatively reliable.

Table 3. Relative heats of formation ($\Delta\Delta H_f$) (kcal mol^{-1}) and $<S^2>$ expectation values computed with AM1/UHF for the closed-shell molecules and open-shell intermediates

	$2 \times C_{60}$	**1** (D_{2h})	**3** (D_{2h})	**2** (C_{2h})	**4** (C_{2v})
$\Delta\Delta H_f$	0	−42.2	−6.0	−14.6	−17.0
$<S^2>$	9.84	10.87	11.07	11.42	10.87

Thermodynamic considerations

The question that arises is: if dimer **1** is so much more stable than C_{60} and the barrier to dimerization is so low, why does spontaneous dimerization not occur? Moreover, the barrier to isomerization of **1** to **3** is only a few kcal mol^{-1} above the energy of $2 \times C_{60}$. It follows that the three species should be in rapid dynamic equilibrium at moderate temperatures. Evidently, failure to observe the dimer in the gas phase can only be ascribed to unfavorable thermodynamics.

Computations of the thermodynamic properties of fullerenes have been few and have been carried out for the most part with semi-empirical methods, which are of limited reliability as regards the energy differences between the different species and accurate evaluation of their vibrational frequencies. Nevertheless, Slanina and co-workers have applied AM1 convincingly to the equilibrium between graphite and C_{60} and C_{70} and to the effect of temperature and pressure on the relative concentrations of the two fullerenes.[6]

Accordingly, THERMO computations (AM1/RHF), were carried out on C_{60} and C_{120} (**1**) over the temperature range 298–900 K. Over this range, the Gibbs free energy of dimerization (ΔG_{dim}) varies smoothly from -18 to $+15$ kcal mol^{-1}. The factor principally responsible for the variation is a relatively rapid decrease in the entropy of dimerization (ΔS_{dim}) with increase in temperature. As a result, the equilibrium constant, which favors the dimer at low temperature, shifts strongly towards the monomer with increase in temperature. The effect on the dimer/monomer ratio is mitigated by the increase in the vapor pressure of C_{60}, but the concentration ratio remains very low throughout the thermally accessible range, as is clear from the data in Table 4.

THERMO computations also indicate that that the free energy difference between dimers **3** and **1** is essentially independent of temperature, remaining close to 35 kcal mol^{-1}. At 900 K the ratio of partial pressures is of the order of 10^{-9}, so the equilibrium concentration of the 'window isomer' would be completely negligible. Evidently, in order to isolate either isomer in the vapor phase, it would have to be formed in a high-temperature non-equilibrium process and then cooled very rapidly, say in a supersonic jet, so as to prevent equilibration.

Table 4. Temperature dependence of K_p and the C_{120}/C_{60} ratio

T (K)	$p(C_{60})$ (atm)[a]	K_p (atm)[b]	R[c]
300	5.77×10^{-25}	9.32×10^{12}	5.41×10^{-12}
400	2.45×10^{-17}	7.32×10^{6}	1.79×10^{-10}
500	9.25×10^{-13}	1.40×10^{3}	1.30×10^{-9}
600	1.04×10^{-9}	4.28	6.05×10^{-9}
700	1.57×10^{-7}	6.53×10^{-2}	1.02×10^{-8}
800	6.79×10^{-6}	2.73×10^{-3}	1.84×10^{-8}
900	1.27×10^{-4}	2.26×10^{-4}	2.86×10^{-8}

[a] Ref. 7.
[b] $K_p = p(C_{120})/p^2(C_{60})$.
[c] $R = K_p \times p(C_{60})$.

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